Studies on Analytical Methods for Trace Elements in Metals by Using Radioactive Isotope. IV : Determination of Aluminium with Calcium-45 Type Cation Exchanger

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Determination of Aluminium with Calcium-45 Type Cation Exchanger*

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Synopsis

Aluminium was determined radiometrically by using calcium-45 isotope and cation exchange resin. The sample solution containing Al^{3+} was adjusted to pH 3.0~4.0 and was treated with the cation exchanger of Ca-R type labeled with calcium-45. The radioactivity of eluted calcium was exactly equivalent to the amount of aluminium ion present. Interferences of ferrous iron, magnesium ion and ammonium ion were examined, and no serious effect was observed. This method was applied to the determination of aluminium in carbon steel, and the results obtained agreed with those by photometric method.

I. Introduction

Aluminium in carbon steels can be determined by the gravimetric, the volumetric and the spectrophotometric method; usually, the spectrophotometric method (oxine-organic solvent extraction method[1] or aluminon method[2]) is used.

M. Honda reported the separation of aluminium and beryllium by using the cation exchanger and calcium chloride solution as eluent.[3] H. Kakihana separated aluminium from other elements by using the cation exchanger of calcium type and calcium chloride solution[4]. Further, the equilibrium constant of aluminium to calcium is calculated as 1.4 in 0.1 N aluminium and 5.6 in 0.01 N aluminium[5]. So it seems possible that effluting the solution containing aluminium through the calcium type cation exchanger column which is labeled with calcium-45, aluminium is exchanged equivalently by the calcium ion (containing radioactive calcium nuclide), and that small amount of aluminium can be determined by measuring the radioactivity in the effluent. Hence, in the present study, it was attempted to determine aluminium radiometrically by using the radioactive isotope calcium-45.

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* The 948th report of the Research Institute for Iron, Steel and Other Metals. Reported in Japanese in the Journal of Japan Institute of Metals, **23** (1959), 367.

(1) Y. Kakita and Y. Yokoyama, Japan Analyst, **2** (1953), 106.
(2) W.E. Thrum, Ind. Eng. Chem., Anal. Ed. **2** (1930), 8.
(3) M. Honda, J. Chem. Soc. Japan, Pure Chem. Sec. **71** (1950), 118.
(4) H. Kakihana, ibid., **72** (1951), 200.
(5) M. Honda, H. Kakihana and Y. Yosino, *Ion Exchange Resin*, Hirokawa Book Company, Tokyo, Japan, (1955), 65.

II. Apparatus and reagent

1. Counter and scaler

The sample was mounted on the stainless steel dish, and the radioactivity of the sample was measured by the decimal scaler in combination with β-ray counting Geiger-Müller tube.

2. Ion exchange resin

1.5 to 2.0 g of cation exchanger in air-dried state (Diaion SK #1, 40~60 mesh) was used, and the resin was mounted in the usual type of glass column (1 cm in diameter), and the apparatus is shown in Fig. 1. The latter apparatus enabled us to treat a large amount of sample solution, and it was easier to control the flow rate by this apparatus than by usual type of column.

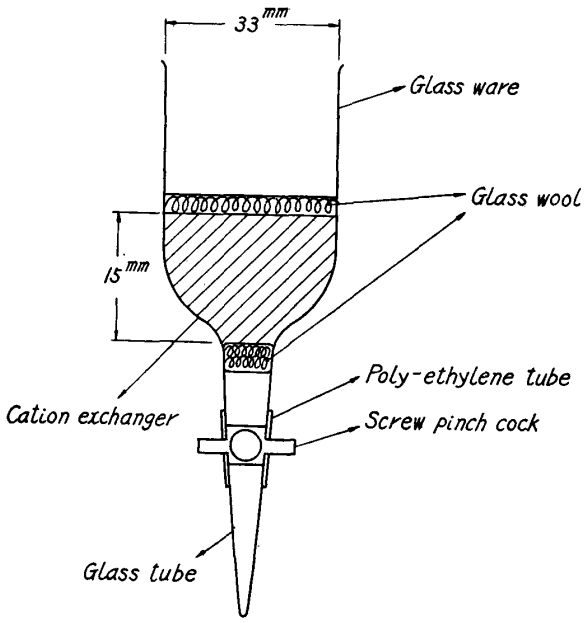

Fig 1. The shape of ion exchange column.

3. Calcium-45 tracer solution

Calcium-45 tracer was prepared from irradiated unit calcium-45 as follows: To the irradiated unit calcium-45 was added calcium carrier, which precipitated as calcium oxalate and was ignited into calcium carbonate. Finally, calcium carbonate was dissolved in hydrochloric acid and diluted to suitable volume.

4. Aluminium standard solution

Aluminium metal of 99.99 per cent purity was dissolved in hydrochloric acid to the concentration of 1mg aluminium in 1 ml of solution. From this solution, several solutions of various concentrations were made.

5. Calcium standard solution.

Standard calcium solution was prepared from Merk's calcium carbonate by dissolving in the hydrochloric acid to the concentration of 9.75mg per ml. This mother solution was diluted according to purposes.

All the other reagents used were of chemically pure grade or of analytically pure grade.

III. Experiments and results

1. An equivalent relation between aluminium and calcium

The equivalent relation between aluminium and calcium was examined. Through the cation exchanger column which was set to acid type and washed well with water was passed the neutral solution of calcium chloride labeled with calcium-45 (specific activity of 5000 cpm/ml), and the resin was converted to

calcium type. After sufficient washing with water, about 50 ml of aluminium solution adjusted to pH 3.4~4.0 was passed through the column at the flow rate of 2 ml per minute. The column was washed with water of equal volume, and the calcium in the effluent and washing solution was precipitated as calcium oxalate. The precipitate was filtered by the filtering apparatus, and washed successively with hot water, ethyl alcohol and the mixture of ethyl alcohol and ether. Then the activity of precipitate was measured together with filter paper.

The activity of calcium corresponding to the amount of aluminium 2~10 mg was plotted in Fig. 2. It was found that aluminium could be exchanged by calcium equivalently.

Table 1 shows the results, in which the amounts of aluminium were taken below 1 mg range in 20 ml of sample solutions. The activities of samples were measured after the evaporation of effluent, and the specific activities of original calcium solution were changed in three steps, namely, 2000, 5000 and 10,000 cpm/ml. The activity of calcium eluted was 14.5 cpm corresponding to 0.02 mg of aluminium by using 2000 cpm/ml calcium chloride solution; 17.7 cpm to 0.005 ml of aluminium by using 5000 cpm/ml solution; and 14.2 cpm to 0.001 mg of aluminium by using 10,000 cpm/ml solution. From these experimental results it is seen

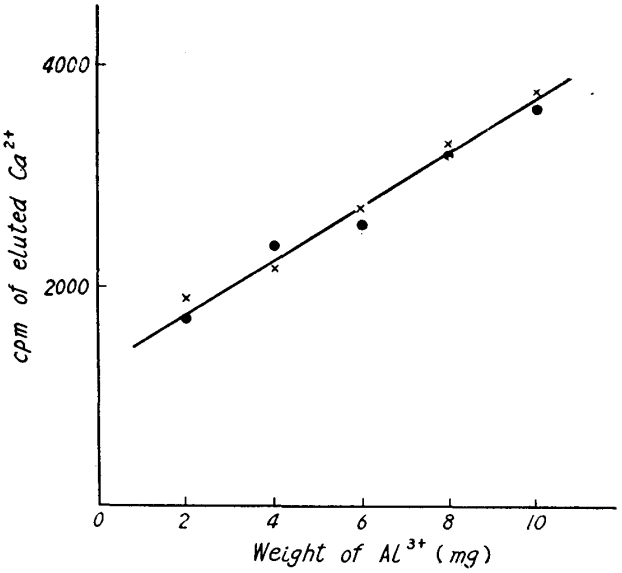

Fig. 2. Relation between amounts of Al^{3+} and cpm of eluted Ca^{2+}.

Table 1. Relation between small amounts of Al^{3+} and cpm of eluted Ca^{2+} when the specific activity of Ca-45 solution was varied.

Al^{3+} taken (mg)	Original cpm of Ca-45 solu. which labeled the resin (cpm/ml)		
	2000	5000	10000
1.0	879.3	2224.7	4521.0
0.5	440.2	1123.1	2772.3
0.2	180.5	508.3	1002.4
0.05	49.2	124.4	253.1
0.02	14.5	52.3	100.1
0.01	—*	29.6	49.9
0.005	—*	17.7	25.0
0.001	—*	—*	14.2

—* shows that the measured values almost equal to the background.

that the higher the specific activity of original calcium solution, the lower the measurable amount of aluminium became.

2. Study on the optimum conditions for exchange between aluminium and calcium

As the above-mentioned experiments were carried out under the condition of pH from 3.4 to 4.0, the optimum conditions for the elution of calcium were studied precisely. The column was treated with the labeled calcium standard solution which had the specific activity of 5000 cpm/ml, and the sample solutions containing 1 or 0.5 mg of aluminium in 50 ml were passed through the column, changing pH of the solutions from 1.0 to 5.5.

As shown in Table 2, when pH of the solutions were adjusted between 3.0

Table 2. The effects of pH on the exchange between Al^{3+} sample solution and Ca-type ion exchanger*

pH of Al^{3+} sample solution	cpm of eluted Ca^{2+}	
	Al^{3+} 1.0mg was taken.	Al^{3+} 0.5mg was taken.
1.0	cpm could not measure	
1.5		
2.0	10252.6	11250.2
2.5	4055.3	4500.2
3.0	2222.1	1106.7
3.5	2210.3	1050.6
4.0	2240.2	1112.5
5.5	hydrolysis of Al occurred	

* Exchanger was labeled with Ca-45 standard solution which had specific activity of 5000 cpm/ml.

and 4.0, the counting values of effluent showed no fluctuation, but it increased intensely below pH of 2.5 to the extent in which it was hardly possible to count.

From these results it was seen that pH of the solution had to be controlled between 3.0 and 4.0.

Sometimes an irregular counting was seen in washing water, which might be due to the elution of calcium from resin by bicarbonate ion that was produced with carbon dioxide dissolved in water. So the washing water was always used after boiling, and the irregular counting was eliminated.

3. The collection of eluted calcium

When the amount of aluminium was very small, the amount of calcium exchanged by aluminium also became small. However, the radioactivity of calcium was measurable, when the specific activity of calcium standard solution was high. In this case, the amount of calcium present in the solution became very low. So in order to collect the calcium in the effluent as calcium oxalate precipitate, calcium carrier had to be added. This procedure resulted in self-absorption effect in measuring radioactivity of precipitate. Hence, the condition

to minimize the effect was studied. To several portions of calcium-45 solution which had the radioactivities from 22.5 to 5025 cpm were added various amounts of calcium carrier from 0.5 to 1.5 mg, and the calcium oxalate precipitated. The precipitate was filtered and the radioactivity was measured.

As shown in Table 3, satisfactory results were obtained in all the regions from low to high counting value, when 1.5 mg of calcium carrier was used. This amount of carrier gave 6.15 mg of calcium oxalate dihydrate, and the thickness of sample was 1.4 mg/cm^2 as calcium oxalate dihydrate. Below this amount of carrier, the counting values were fluctuated because of the un-uniformity of the thickness, resulting from the irregularity of the precipitate particle.

Table 3. The effects of Ca-carrier weights on cpm of calcium oxalate.

Original cpm of Ca solu.	Ca-carrier added (mg)		
	0.5	1.0	1.5
22.5	26.3	23.4	23.3
46.3	46.4	47.3	42.2
108 2	114.3	99.2	97.4
522.5	560.4	532.5	504.3
1033.4	1152.5	1112.4	1009.6
2240.2	2333.2	2292.3	2192.8
5025.3	5125.5	5140.6	5020.4

* The original cpm of Ca-solution was measured after the evaporation of each solution.

From these results it was decided to use 1.5mg of calcium carrier.

4. Effects of diverse ions

Though it was evident that calcium was exchanged by those ions whose valencies are equal to or higher than that of aluminium, only the effects of ferrous iron, magnesium and ammonium were examined.

According to M. Honda[5], the value of K_{Ca}^{Mg} for magnesium was 0.4. It was found from the present experiment that magnesium did not exchange with calcium, and that 2~5 mg of ferrous iron present in 30 ml of solution does not affect the method, as seen in Table 4. This fact can be explained as being the poor ability of absorption of ferrous iron on the resin, which has been reported by Kakihana et al.[6]

Ammonium ion entered into the solution during the neutralization process, and it is reasonable to think that an exchange of ammonium with calcium was caused. So the effects of ammonium ion were examined in the concentration range 0.15~4.0 M. As shown in Table 4, the activity of effluent increased suddenly at the concentration 4.0 M of ammonium ion, and it seemed necessary to control the amount of ammonium ion below 3.0 M in neutralizing process.

(6) H. Kakihana and M. Kozima, Japan Analyst, **2** (1953), 421.

Table 4. Effects of other elements.

*1 Elements taken (mg)		cpm of elution *2	
		Al 1.0mg was taken.	Al 0.5mg was taken.
Fe^{2+}	0.5	2250.0	1068.5
	1.0	2212.6	1099.4
	2.0	2243.7	1160.3
	5.0	2302.6	1121.4
	6.0	2487.6	1340.4
Mg^{2+}	5.0	2232.5	1120.6
NH_4^+	81	2224.8	1118.2
	162	2214.2	1109.3
	540	2240.9	1132.5
	810	2233.3	1121.2
	1620	2193.5	1122.8
	2160	2687.9	1542.5

*1 The weight of elements shows the amount of it which exists in 30 ml of sample solution.

*2 Exchanger was labeled with Ca-45 standard solution which had specific activity of 5000 cpm/ml.

5. Preparation of calibration curve

The calibration curve was prepared as follows: Acid type resin was converted to calcium type with the labeled calcium standard solution (5000 cpm/ml), and washed with water. A suitable aliquot of aluminium standard solution containing 0.05~0.5 mg of alminium was pipetted into the beaker, and was diluted to nearly 50 ml with water and the pH was adjusted to 3.5. (It was necessary to see to it that the ammonium ion concentration will not exceed 3.0 N.) The solution was passed through the column at the rate 2 ml per-minute. The column was washed with water which is free from carbon dioxide by boiling. The effluent was heated, and 10 ml of 5 per cent ammonium oxalate solution was added. The solution was made alkaline with the acid of methyl orange as an indicator by adding ammonium hydroxide dropwise. When no precipitate was produced, 1.5 mg of calcium carrier was added. After the precipitate was settled, it was filtered with the aid of suction. The precipitate was washed successively with hot water, alcohol and mixture of alcohol and ether.

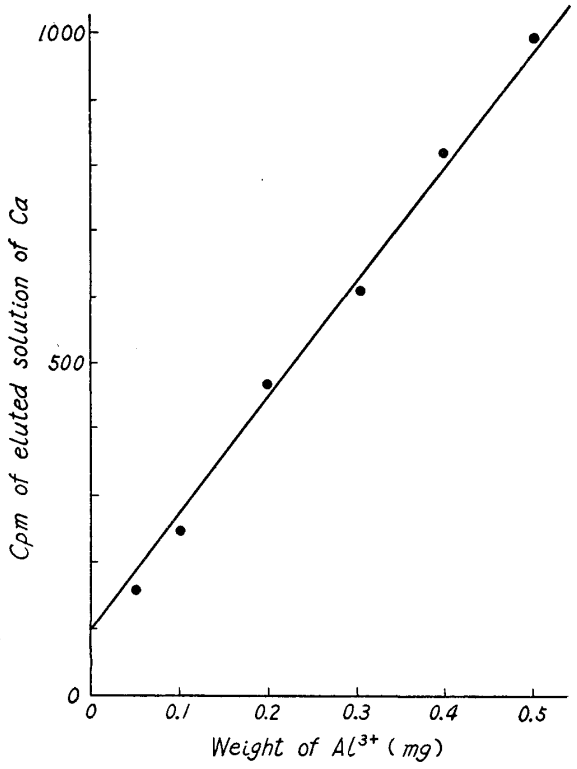

Fig. 3. Calibration curve of Al^{3+}.

The precipitate and the filter paper were tran sferred to the counting dish, and the activity was measured. The activity was plotted versus the amount of aluminium taken. As shown in Fig. 3, aluminium amount and calcium activity shows a linear relation.

6. Results of actual analysis

The above-mentioned method was applied to the analysis of aluminium in carbon steel.

1 g of steel sample was dissolved with 20 ml of hydrochloric acid (1+1) and the solution was heated. After the completion of the dissolution, the solution was evaporated to dryness, the residue in the beaker was leached with 30 ml of 6 N hydrochloric acid, and the silica was removed rapidly. The filtrate was treated with equal volume of ether, and iron was separated from aqueous layer. After ether extraction, ether was expelled from the residual solution by gentle heating. Then the solution was evaporated to 20 ml, and the iron still remaining was reduced to di-valent state by passing the sulfur dioxide through the solution. The volume of solution was filled to 50 ml, and pH of the solution was adjusted to 3.5. The solution was then treated in the same way as mentioned in the preparation of calibration curve, and the amount of aluminium was determined from the calibration curve.

The results obtained with several samples are shown in Table 5, which are

Table 5. Results of actual analysis.

Sample	Radiometric method (%)	Oxine-benzene extraction method (%)
Carbon steel	0.02_1	0.019
〃	0.03_2	0.027
Carbon steel + Al	0.03_4	0.030

in good agreement with the values determined spectrophotometrically by using the oxine-benzene extraction method.

Summary

(1) The cation exchanger was set up to calcium type by calcium standard solution labeled with calcium-45, and the sample solution containing aluminium was passed through this column. Aluminium was determined by measuring the activity of calcium in effluent which exchanged aluminium ion.

(2) From the optimum conditions of aluminium ion for calcium ion it was seen that the exchange took place quantitatively at the pH 3.0~4.0. Selecting the suitable calcium standard solution of specific activity, aluminium could be determined over a wide range from 0.001 to 10 mg.

(3) When the amount of calcium was very small, non-radioactive calcium was added as an isotopic carrier so as to give about 5 mg of calcium oxalate dihydrate.

(4) The interferences of ferrous iron, magnesium ion and ammonium ion were

examined. Of these ions, magnesium ion showed no interference, ferrous iron had no effect on the method up to the amount of 5 mg in 30 ml of the solution, and ammonium ion showed no interference below 3 M of its concentration.

(5) The method was applied to determine the aluminium content in carbon steel, and the results were satisfactory, compared with those obtained spectrophotometrically.

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